

REPORT DOCUMENTATION PAGEForm Approved
OMB No. 0704-0188

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1. REPORT DATE (DD-MM-YYYY) 05-09-2003		2. REPORT TYPE Technical Paper		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Polyazide Chemistry. Preparation and Characterization of $\text{Te}(\text{N}_3)_4$ and $[\text{P}(\text{C}_6\text{H}_5)_4]_2[\text{Te}(\text{N}_3)_6]$				5a. CONTRACT NUMBER F04611-99-C-0025	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Ralf Haiges (Loker Research Institute); Jerry A. Boatz (AFRL/PRSP); Michael Gerken, Stefan Schneider, Thorsten Schroer (Loker Research Institute); Karl O. Christe (ERC)				5d. PROJECT NUMBER DARP	
				5e. TASK NUMBER A205	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) ERC, Inc. 10 East Saturn Blvd. Edwards AFB CA 93524-7680 Loker Research Institute University of Southern California Los Angeles CA 90089-1661				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-7048				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S NUMBER(S) AFRL-PR-ED-TP-2003-222	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.					
13. SUPPLEMENTARY NOTES For presentation in the Journal Angewandte Chemie.					
14. ABSTRACT					
<div style="border: 1px solid black; padding: 10px; display: inline-block;">20031017 128</div>					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT Unclassified			A	22	Leilani Richardson
b. ABSTRACT Unclassified					
c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (include area code) (661) 275-5015		

Polyazide Chemistry. Preparation and Characterization of $\text{Te}(\text{N}_3)_4$ and $[\text{P}(\text{C}_6\text{H}_5)_4]_2[\text{Te}(\text{N}_3)_6]$ ^{**}

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The azido-group is highly energetic and adds about 70 kcal/mol to the energy content of a molecule. It is, therefore, not surprising that polyazides are highly endothermic compounds, and that their energy content increases with an increasing number of azido ligands. Compared to the relatively stable azide anion, which possesses two double bonds, the bonds in covalent azides are polarized towards a single and a triple bond, which greatly facilitates N_2 elimination and enhances their shock sensitivity.



Consequently, the synthesis and characterization of covalent, binary azides containing multiple azido ligands can present great experimental challenges, and binary tellurium azides are no exemption to this general rule.

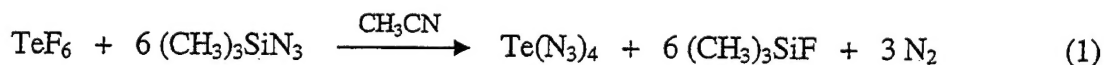
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[**] This work was funded by the Defense Advanced Research Projects Agency, with additional support from the Air Force Office of Scientific Research and the National Science Foundation. R.H. thanks the Deutsche Forschungsgemeinschaft for a postdoctoral fellowship. We thank Drs. A. Morrish, D. Woodbury, and M. Berman, for their steady support, and Drs. R. Wagner, I. Tsyba, and Prof. R. Bau for their help and stimulating discussions. We also thank Prof. T. Klapoetke and his colleagues for exchange of information about their independent syntheses of $\text{Te}(\text{N}_3)_4$ and $\text{Te}(\text{N}_3)_5^-$.

Whereas numerous, partially azide substituted tellurium compounds have been reported,^[1-14] only one binary tellurium azide, the $\text{Te}(\text{N}_3)_3^+$ cation, has previously been reported.^[5] In this paper, we wish to communicate the synthesis and characterization of two novel binary tellurium azides, $\text{Te}(\text{N}_3)_4$ and $[\text{Te}(\text{N}_3)_6]^{2-}$.

In the presence of catalytic amounts of CsF, the reaction of TeF_6 with excess $(\text{CH}_3)_3\text{SiN}_3$ in acetonitrile solution at room temperature results in the reduction of Te(VI) to Te(IV), while the azide ion is oxidized to dinitrogen. Furthermore, complete fluoride-azide exchange takes place, yielding a clear yellow solution of $\text{Te}(\text{N}_3)_4$ according to Eq. (1).



Removal of the volatile products, (CH_3CN) , $(\text{CH}_3)_3\text{SiF}$ and excess $(\text{CH}_3)_3\text{SiN}_3$, at ambient temperature results in the isolation of $\text{Te}(\text{N}_3)_4$ as a bright yellow solid. In the absence of CsF, no fluoride-azide exchange reaction was observed even after several days at ambient temperature. The catalytic function of the fluoride ion in these reactions probably involves the generation of intermediate free azide ions from the reaction of $(\text{CH}_3)_3\text{SiN}_3$ with F^- , and these free azide ions might be the actual reagent. The need for fluoride ion catalysis, found in our study, is in contrast to the results from a previous ^{19}F NMR study^[9] in which TeF_6 was reported to undergo facile fluoride-azide exchange with $(\text{CH}_3)_3\text{SiN}_3$ in CD_3CN solution, producing all members of the

$\text{TeF}_n(\text{N}_3)_{6-n}$ ($n = 1-5$) series. In their study, these authors also observed the reduction of Te(VI) to Te(IV) by azide ion as a side reaction.

As expected for a highly endothermic, binary, covalent polyazide, $\text{Te(N}_3)_4$ is very sensitive and can explode violently. Its identity was established by the observed material balance, and vibrational and NMR spectroscopy. The presence of a single $\delta(^{125}\text{Te})$ signal at 1427 ppm and the absence of any signals exhibiting Te-F spin-spin coupling in CH_3CN solution at 25 °C confirm complete fluoride-azide exchange. The observed ^{125}Te shift of 1427 ppm is in accord with our expectations for a multi-azido substituted Te(IV) compound. Thus, the shift reported for the closest known analogue, $\text{CH}_3\text{Te(N}_3)_3$, is 1405 ppm.^[12] Furthermore, the presence of covalent azido ligands^[11-16] is confirmed by the observed ^{14}N NMR shifts of -150.9 ppm (N_β , $\Delta\nu_{1/2} = 100$ Hz), -235.3 ppm (N_γ , $\Delta\nu_{1/2} = 163$ Hz), -288 ppm (N_α , $\Delta\nu_{1/2} \sim 500$ Hz) in CH_2Cl_2 solution at 25 °C. In addition to quadrupolar broadening, rapid ligand exchange on the NMR timescale by the Berry pseudo-rotation mechanism^[17] might contribute to the observation of only one set of azide signals and the relatively broadness of the line for the N_β resonance.

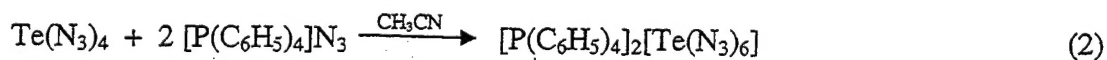
The observed Raman spectrum of solid $\text{Te(N}_3)_4$ is shown in Figure 1, and the observed infrared and Raman frequencies and intensities are summarized in Table 1. Assignments of the observed spectra were made by a comparison with those calculated at the B3LYP/SBKJC+(d) level of theory.^[18]

These calculations resulted in two minimum energy structures of C_2 symmetry (Figures 2a and 2b). Both structures are derived from pseudo-trigonal bipyramids, in which one of the equatorial positions is occupied by the sterically active free valence electron pair of tellurium. The two structures differ in energy by only 1.8 kcal/mol. Their main difference is the orientation of the axial azido ligands. In Figure 2a, the axial azido ligands point in the same direction and

toward the free valence electron pair on Te. This compresses the free pair in the axial direction and exerts additional pressure on the two equatorial ligands, compressing their bond angle by 11° compared to structure 2b in which the axial azido ligands point in different directions and away from the free pair.

The vibrational spectra, calculated for 2a and 2b (Table 1), are also almost identical and, therefore, do not permit a distinction between the two models. Nevertheless, they strongly support the presence of highly covalent azido ligands, the absence of Te-F bonds, and the identification of this compound as $\text{Te}(\text{N}_3)_4$. For the different isomers, the Te-N skeletal geometries are very similar, and the isomers differ only in the orientation of the highly fluxional azido ligands. Therefore, the vibrational spectra should differ mainly in the torsional modes, but these modes are difficult to observe because of their low frequencies and intensities. This problem might be further complicated in the solid state, where coordinatively unsaturated polyazides exhibit a tendency to form nitrogen bridges. Consequently, a distinction of isomers based on the observed Te-N skeletal modes is very difficult, and more reliable methods, such as crystal structure data, are required.

The reaction of $\text{Te}(\text{N}_3)_4$ with ionic azides leads to the formation of the $[\text{Te}(\text{N}_3)_6]^{2-}$ anion, according to Eq. (2).



The $[\text{P}(\text{C}_6\text{H}_5)_4]_2[\text{Te}(\text{N}_3)_6]$ salt is a yellow solid which is stable at room temperature and, because of the presence of two large counter-ions, is much less sensitive to shock than $\text{Te}(\text{N}_3)_4$. It was characterized by its crystal structure,^[19] infrared and Raman spectroscopy, and its ^{125}Te and ^{14}N NMR spectra.

$[\text{P}(\text{C}_6\text{H}_5)_4]_2[\text{Te}(\text{N}_3)_6]$ crystallizes in the triclinic space group $P\bar{1}$ and is the first structurally characterized anionic tellurium-(IV) azide.^[20] The structure of the dianion is shown in Figure 3 and consists of a TeN_6 skeleton that is strongly distorted from octahedral symmetry by the sterically active free valence electron pair on tellurium. If the free electron pair on Te were sterically inactive, one would expect for a $\text{Te}(\text{N}_3)_6$ species perfect S_6 symmetry, as predicted by our theoretical studies for $\text{Te}(\text{N}_3)_6$ and $[\text{Te}(\text{N}_3)_6]^{2-}$ (Figure 4). The possibility of the distortion in $[\text{Te}(\text{N}_3)_6]^{2-}$ being caused by nitrogen bridging with other anions can be ruled out because, in its $\text{P}(\text{C}_6\text{H}_5)_4^+$ salt, the anions are well separated by twice as many large counter-ions, and the closest Te-N contacts between neighboring anions are 6.2 Å.

From the bond angles, observed for $[\text{Te}(\text{N}_3)_6]^{2-}$, it appears that the free pair is located primarily between the N10 and N16 atoms (widening of the N10-Te-N16 angle to $120.36(8)^\circ$) and displaced somewhat toward N4. Therefore, the $[\text{Te}(\text{N}_3)_6]^{2-}$ structure is best described as a distorted pseudo pentagonal-bipyramid in which the free valence electron pair of tellurium is sterically active and occupies one of the equatorial positions. Because of increased ligand crowding in the equatorial plane, the free pair is located somewhat above the N1-N7-N10-N16 plane. This interpretation of the structure is also supported by the observed Te-N bond distances which exhibit remarkable differences and can be separated into three sets of pairs: N1 [2.133(2)] and N7 [2.093(2)], N4 [2.241(2)] and N13 [2.199(2)], and N10 [2.419(2)] and N16 [2.530(2)] Å. The N1-N2-N3 and N7-N8-N9 ligands are highly covalent, as shown by their very short Te-N distances of about 2.1 Å and the large differences between the $\text{N}_\alpha\text{-N}_\beta$ and $\text{N}_\beta\text{-N}_\gamma$ bonds. In contrast, the N16-N17-N18 ligand is half-ionic with a Te-N bond distance of 2.530(2) Å and similar $\text{N}_\alpha\text{-N}_\beta$ and $\text{N}_\beta\text{-N}_\gamma$ bond distances.

By contrast to the observed crystal structure, the global minimum energy structure, predicted for free gaseous $[\text{Te}(\text{N}_3)_6]^{2-}$ at the B3LYP/SBKJC+(d) level of theory,^[18] shows ideal S_6 symmetry (Figure 4). Local minima of C_1 symmetry with asymmetric arrangements of the azido groups were also found which are only slightly higher in energy. The distortions in these C_1 structures are relatively minor and are caused by mutual repulsion effects among the azido ligands. These findings indicate that in our calculations the free valence electron pair on Te is sterically inactive. Similar problems with correctly predicting the steric activity of free valence electron pairs by these methods have been encountered by us for related species, such as IF_6^- . This ion is known to have a sterically active free valence electron pair and a strongly distorted octahedral structure,^[21,22] but the theoretical studies predict an ideal octahedral structure with a sterically inactive free valence electron pair.^[23]

The NMR spectra provide further support for the presence of the $[\text{Te}(\text{N}_3)_6]^{2-}$ anion. The observed ^{125}Te shift of 1250 ppm in CH_3CN solution at 25 °C is in the range expected for a covalent multi-azido substituted Te(IV) compound (see above) and, relative to $\text{Te}(\text{N}_3)_4$, its shielding is increased by 177 ppm due to the addition of two negatively charged azide ions. By analogy with $\text{Te}(\text{N}_3)_4$, the ^{14}N spectra in CH_2Cl_2 solution at 25 °C show resonances characteristic for covalent azido groups at -141.9 ppm (N_β , $\Delta\nu_{1/2} = 35.4$ Hz), -186.3 ppm (N_γ , $\Delta\nu_{1/2} = 96.7$ Hz), and N_α being too broad for a reliable assignment. Again, the observation of a single set of signals implies rapid exchange of the different type of ligands on the NMR time scale.

The observed infrared and Raman spectra of $[\text{P}(\text{C}_6\text{H}_5)_4]_2[\text{Te}(\text{N}_3)_6]$ are shown in Figure 5, and the observed frequencies and those calculated for S_6 symmetry are summarized in Table 2. Again, the agreement between the observed and the calculated spectra is good for the azido vibrations, but, for the skeletal TeN_6 modes, the agreement is poorer because of the failure of the

calculations to properly predict the distortion caused by the steric activity of the free valence electron pair on Te. Despite these complications, the predicted and observed Te-N skeletal vibrations in $[\text{Te}(\text{N}_3)_6]^{2-}$ are markedly lower than those in $\text{Te}(\text{N}_3)_4$, as expected from the increased ionicity of the Te-N bonds.

Tellurium azides are very remarkable because the nature of their Te-N bonds can range for closely related compounds, or even within the same compound, from highly ionic to highly covalent with correspondingly large changes in bond distances. For example, in R_3TeN_3 [$\text{R} = \text{CH}_3$ or C_6H_5],^[14] the Te-N bond distances have average values of about 3.0 Å and the two N-N bonds in the azido groups are practically identical, indicating the presence of highly ionic azides. The other extreme, that is the presence of highly covalent azido ligands, is found in the $\text{Te}(\text{N}_3)_3^+$ cation^[5] and $\text{RTe}(\text{N}_3)_3$ [$\text{R} = \text{C}_2\text{H}_5$, *n*- C_3H_7 , *i*- C_3H_7 , or 2,4,6- $(\text{CH}_3)_3\text{C}_6\text{H}_2$].^[12] In these compounds, the Te-N bond distances range from 1.99 to 2.25 Å, and the $\text{N}_\alpha\text{-N}_\beta$ and $\text{N}_\beta\text{-N}_\gamma$ distances differ by about 0.10 Å. As might be expected, compounds with bond distances, which fall in between these extremes, are also known. For example, the Te-N distance in $[(\text{C}_6\text{H}_5)_2\text{TeN}_3]_2\text{O}$ is 2.397(8) Å.^[10]

Although the bond distances for $\text{Te}(\text{N}_3)_4$ could not be measured experimentally, the values of 2.071 and 2.185 Å, predicted for the free gaseous molecule at the B3LYP/SBKJC+(d) level of theory,^[18] and the observed vibrational and NMR spectra suggest the presence of highly covalent Te-N bonds, similar to those predicted for free $\text{Te}(\text{N}_3)_6$. In contrast, the Te-N distances, observed for $\text{Te}(\text{N}_3)_6^{2-}$, cover a wide range from 2.093(2) to 2.530(2) Å, indicating the simultaneous presence of highly covalent and semi-ionic Te-N bonds within the same ion. The increase of 0.20 Å in the predicted average Te-N bond length on going from $\text{Te}(\text{N}_3)_6$ to

$[\text{Te}(\text{N}_3)_6]^{2-}$ can be explained by a higher ionicity of the Te-N bonds in $[\text{Te}(\text{N}_3)_6]^{2-}$, caused by the two formal negative charges.

Experimental Section

Caution! Covalent azides are potentially hazardous and can decompose explosively under various conditions! They should be handled only on a small scale with appropriate safety precautions (face shields, leather gloves and protective clothing).

All reactions were carried out in Teflon-FEP ampules closed by stainless steel valves. Volatile materials were handled in a stainless steel-Teflon-FEP or Pyrex glass vacuum line. Nonvolatile materials were handled in the dry argon atmosphere of a glove-box. All reaction vessels and the stainless steel line were passivated with ClF_3 prior to use.

Raman spectra were recorded in the range $4000\text{--}80\text{ cm}^{-1}$ on a Bruker Equinox 55 FT-RA spectrophotometer using a Nd-YAG laser at 1064 nm. Pyrex melting point tubes that were baked out at $300\text{ }^\circ\text{C}$ for 48 h at 10 mTorr vacuum or Teflon-FEP tubes with stainless steel valves that were passivated with ClF_3 were used as sample containers. Infrared spectra were recorded on a Midac, M Series, FT-IR spectrometer using KBr or AgCl pellets. The pellets were prepared inside the glove-box using an Econo press (Barnes Engineering Co.). NMR spectra were recorded unlocked at 500.13 MHz (^1H), 125.76 MHz (^{13}C), 202.46 MHz (^{31}P), 158.03 MHz (^{125}Te) and 36.13 MHz (^{14}N) on a Bruker AMX 500 spectrometer using solutions of the compounds in acetonitrile or dichloromethane in sealed standard glass tubes. Neat TMS (0.00 ppm) was used as external reference for ^1H and ^{13}C , 85 % aqueous H_3PO_4 (0.00 ppm) as external reference for ^{31}P , saturated aqueous $\text{Te}(\text{OH})_6$ (710.9 ppm)^[24] as external reference for ^{125}Te and neat CH_3NO_2 (0.00 ppm) was the external reference for ^{14}N .

The starting materials TeF_6 (Ozark Mahoning) and $[(\text{C}_6\text{H}_5)_4\text{P}]\text{I}$ (Aldrich) were used without further purification. The $(\text{CH}_3)_3\text{SiN}_3$ (Aldrich) was purified by fractional condensation prior to use. Solvents were dried by standard methods and freshly distilled prior to use. $[(\text{C}_6\text{H}_5)_4\text{P}]\text{N}_3$ was prepared from $[(\text{C}_6\text{H}_5)_4\text{P}]\text{I}$ and AgN_3 .

Preparation of $\text{Te}(\text{N}_3)_4$: On the stainless steel vacuum line, TeF_6 (0.438 mmol) was condensed at -196°C into a Teflon-FEP ampule containing a small amount of CsF (0.05 mmol). The ampule was then attached to a glass vacuum line and after evacuation, CH_3CN (50 mmol) and $(\text{CH}_3)_3\text{SiN}_3$ (3.21 mmol) was condensed in at -196°C . The mixture was allowed to warm to ambient temperature, resulting in weak gas-evolution and a yellow color of the solution. After 8 h, the temperature was lowered to -20°C , and all volatile compounds were pumped off over a period of 8h, leaving behind a yellow liquid. Additional pumping at ambient temperature for 2 h resulted in a bright yellow solid (0.130 g, weight calculated for 0.438 mmol $\text{Te}(\text{N}_3)_4 = 0.129$ g). Inspection of the volatile material trapped at -196°C by gas-FTIR spectroscopy showed CH_3CN and $(\text{CH}_3)_3\text{SiF}^{[25,26]}$ as the sole reaction by-product. The solid residue was identified by vibrational and NMR spectroscopy as $\text{Te}(\text{N}_3)_4$.

Preparation of $[(\text{C}_6\text{H}_5)_4\text{P}]_2[\text{Te}(\text{N}_3)_6]$: $[(\text{C}_6\text{H}_5)_4\text{P}]\text{N}_3$ (0.6 mmol) was loaded into a Teflon-FEP ampule containing $\text{Te}(\text{N}_3)_4$ (0.3 mmol), followed by the addition of CH_3CN (30 mmol) *in vacuo* at -196°C . The mixture was warmed to room temperature, resulting in the formation of an orange solution. After 3 h, all volatile material was pumped off, leaving behind an orange solid (0.310 g, weight calculated for 0.3 mmol $[(\text{C}_6\text{H}_5)_4\text{P}]_2[\text{Te}(\text{N}_3)_6] = 0.317$ g). Single crystals were grown from a solution in CH_3CN . The compound was characterized by vibrational and NMR spectroscopy and its crystal structure.

Keywords: Crystal structure, Tellurium azides, Vibrational spectra, NMR spectra, Theoretical calculations

References

- [1] N. Wiberg, G. Schwenk, K. H. Schmid, *Chem. Ber.* **1972**, *105*, 1209.
- [2] R. F. Ziolo, K. Pritchett, *J. Organometal. Chem.* **1976**, *116*, 211.
- [3] a) T. N. Srivastava, R. C. Srivastasa, M. Singh, *J. Organometal. Chem.* **1978**, *157*, 405;
b) T. N. Srivastava, R. C. Srivastasa, H. B. Singh, *Indian J. Chem.* **1979**, *18a*, 71; c) T. N. Srivastava, R. C. Srivastasa, H. B. Singh, M. Singh, *Indian J. Chem.* **1979**, *18a*, 367.
- [4] P. Raj, K. Singhal, R. Rastogi, *Tetrahedron*, **1986**, *5*, 677.
- [5] J. P. Johnson, G. K. MacLean, J. Passmore, P. S. White, *Can. J. Chem.* **1989**, *67*, 1687.
- [6] P. C. Srivastava, A. Trivedi, *Indian J. Chem.* **1989**, *28a*, 1110.
- [7] W. Fimml, F. Sladky, *Chem. Ber.* **1991**, *124*, 1131.
- [8] R. Choukroun, Y. Raoult, D. Gervais, *J. Organometal. Chem.* **1990**, *391*, 189.
- [9] I. B. Gorrell, C. J. Ludman, R. S. Matthews, *J. Chem. Soc., Dalton Trans.* **1992**, 2899.
- [10] P. Magnus, M. B. Roe, V. Lynch, C. Hulme, *J. Chem. Soc., Chem. Commun.* **1995**, 1609.
- [11] T. M. Klapoetke, B. Krumm, P. Mayer, O. P. Ruscitti, *Inorg. Chem.* **2000**, *39*, 5426.
- [12] T. M. Klapoetke, B. Krumm, P. Mayer, H. Piotrowski, O. P. Ruscitti, A. Schiller, *Inorg. Chem.* **2002**, *41*, 1184.
- [13] W. Fraenk, T. M. Klapoetke in *Inorganic Chemistry Highlights* (Eds.: G. Meyer, D. Naumann, L. Wesemann) Wiley-VCH, Weinheim, Germany, **2002**.
- [14] T. M. Klapoetke, B. Krumm, P. Mayer, H. Piotrowski, I. Schwab, M. Vogt, *Eur. J. Inorg. Chem.* **2002**, 2701.

- [15] J. Mason in *Multinuclear NMR* (Ed.: J. Mason) Plenum Press, New York, 1987.
- [16] S. Berger, S. Braun, H. O. Kalinowski, *NMR Spectroscopy of the Non-Metallic Elements*, John Wiley & Sons, Chichester, England, 1997.
- [17] R. S. Berry, *J. Chem. Phys.* **1960**, 32, 933.
- [18] The molecular structures and vibrational frequencies were calculated at the DFT level using the B3LYP hybrid functional (A. D. Becke, *J. Chem. Phys.* **1993**, 98, 5648; P. J. Stephens, F. J. Devlin, C. F. Chabrowski, M. J. Frisch, *J. Phys. Chem.* **1994**, 98, 11623; R. H. Hertwig, W. Koch, *Chem. Phys. Lett.* **1997**, 268, 345), which included the VWN5 correlation functional (S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, 58, 1200). The SBKJC effective core potential (W. J. Stevens, H. Basch, M. Krauss, *J. Chem. Phys.* **1984**, 81, 6026; W. J. Stevens, M. Krauss, H. Basch, P. G. Jasien, *Can. J. Chem.* **1992**, 70, 612) and the corresponding valence-only basis set augmented with d polarization functions (the d function exponents for Te and N are 0.237 and 0.8, respectively; see "Gaussian Basis Sets for Molecular Calculations", S. Huzinaga, J. Andzelm, M. Klobukowski, E. Radzio-Andzelm, Y. Sakai, H. Tatewaki, Elsevier, Amsterdam, 1984, and P. C. Hariharan and J. A. Pople, *Theoret. Chim. Acta* **1973**, 28, 213) and a diffuse s+p shell on each atom (the diffuse s+p exponents for Te and N are 0.0306 and 0.0639, respectively; see T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. von R. Schleyer, *J. Comput. Chem.* **1983**, 4, 294) were used, denoted as B3LYP/SBKJC+(d). All calculations were performed using GAMESS (M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, J. A. Montgomery, *J. Comput. Chem.* **1993**, 14, 1347).

- [19] Crystal data for C₄₈H₄₀N₁₈P₂Te: $M_r = 1058.52$, triclinic, space group $P\bar{1}$, $a = 10.1938(11)$, $b = 15.1642(16)$, $c = 15.9217(17)$ Å, $\alpha = 78.777(2)$, $\beta = 88.419(2)$, $\gamma = 78.317(2)^\circ$, $V = 2363.9(4)$ Å³, $F(000) = 1072$, $\rho_{\text{calcd.}} (Z = 2) = 1.487 \text{ g cm}^{-3}$, $\mu = 0.754 \text{ mm}^{-1}$, approximate crystal dimensions $0.19 \times 0.14 \times 0.04 \text{ mm}^3$, θ range = 1.30 to 27.50° , $\text{MoK}\alpha$ ($\lambda = 0.71073$ Å), $T = 85 \text{ K}$, 14284 measured data (Bruker 3-circle, SMART APEX CCD with χ -axis fixed at 54.74° , using the SMART V 5.625 program, Bruker AXS: Madison, WI, 2001), of which 9964 ($R_{\text{int}} = 0.0216$) unique. Lorentz and polarization correction (SAINT V 6.22 program, Bruker AXS: Madison, WI, 2001), absorption correction (SADABS program, Bruker AXS: Madison, WI, 2001). Structure solution by direct methods (SHELXTL 5.10, Bruker AXS: Madison, WI, 2000), full-matrix least-squares refinement on F^2 , data to parameters ratio: 16.0 : 1, final R indices [$I > 2\sigma(I)$] : $R_I = 0.0357$, $wR_2 = 0.0891$, $R_I = 0.0406$, $wR_2 = 0.0919$ (all data), GOF on $F^2 = 1.059$. Further crystallographic details can be obtained from the Cambridge Crystallographic Data Centre (CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk) on quoting the deposition no. CCDC-217066.
- [20] In an independent study, T. M. Klapoetke, B. Krumm, P. Mayr, and I. Schwab (see preceding or following paper) have also obtained a structure of an anionic tellurium(IV) azide, $\text{Te}(\text{N}_3)_5^-$.
- [21] K. O. Christe, W. W. Wilson, *Inorg. Chem.* **1989**, 28, 3275.
- [22] A. R. Mahjoub, K. Seppelt, *Angew. Chem. Int. Ed. Engl.* **1991**, 30, 323.
- [23] D. A. Dixon, K. O. Christe, unpublished results.
- [24] M.J. Collins, G.J. Schrobilgen, *Inorg. Chem.* **1985**, 24, 2608-2614.
- [25] K. Licht, P. Koehler, H. Kriegsmann, *Z. Anorg. Allg. Chem.* **1975**, 415, 31.

[26] H. Bürger, *Spectrochim. Acta* 1968, 24A, 2015.

Table 1: Comparison of Observed and Unscaled Calculated Vibrational Frequencies (cm^{-1}) and Intensities for $\text{Te}(\text{N}_3)_4$.

mode	approx. mode		observed ^[a]		calculated ^[b]	
	description in C_2		IR	Raman	Structure a	Structure b
a	ν_1	$\nu_{\text{as}}\text{N}_3$		2119 [4.3]	2200 (92.9) [381.6]	2200 (147.7) [424.1]
	ν_2	$\nu_{\text{as}}\text{N}_3$	2110 vs	2094 [3.3]	2165 (901.8) [141.6]	2180 (80.3) [456.3]
	ν_3	$\nu_{\text{s}}\text{N}_3$		1312 [0.3]	1284 (105.4) [8.7]	1297 (11.2) [4.0]
	ν_4	$\nu_{\text{s}}\text{N}_3$		1257 [0.4]	1227 (137.2) [1.7]	1223 (73.5) [2.3]
	ν_5	δN_3		649 [1.9]	628 (1.0) [15.8]	629 (0.0) [5.7]
	ν_6	δN_3			622 (3.4) [1.7]	611 (0.2) [10.6]
	ν_7	δN_3			546 (0.0) [1.8]	556 (8.7) [0.2]
	ν_8	δN_3			526 (3.6) [0.7]	523 (7.3) [1.0]
	ν_9	$\nu_{\text{sym}}\text{TeN}_2 \text{ eq}$		424 [10.0]	401 (10.4) [119.1]	394 (8.3) [121.2]
	ν_{10}	$\nu_{\text{sym}}\text{TeN}_2 \text{ ax}$	[c]	343 [4.6]	360 (6.1) [21.3]	355 (2.2) [23.2]
	ν_{11}		[c]	241 [1.1]	234 (19.0) [9.5]	236 (4.5) [18.4]
	ν_{12}		[c]	216 [1.3]	214 (4.8) [15.7]	196 (15.1) [6.7]
	ν_{13}		[c]	183 [1.4]	162 (1.4) [11.8]	159 (0.1) [15.4]
	ν_{14}		[c]	138 [3.4]	130 (0.2) [12.9]	116 (0.4) [2.1]
	ν_{15}		[c]		59 (1.0) [9.6]	84 (0.0) [23.3]
	ν_{16}		[c]		38 (0.5) [16.8]	40 (0.0) [6.5]
	ν_{17}		[c]		28 (0.0) [4.6]	25 (0.7) [5.7]
b	ν_{18}	$\nu_{\text{as}}\text{N}_3$	2110 vs	2094 [3.3]	2187 (833.1) [103.4]	2191 (989.2) [91.7]
	ν_{19}	$\nu_{\text{as}}\text{N}_3$	2060 vs	2070 [2.1]	2141 (1380.5) [207.2]	2162 (1941.3) [41.6]
	ν_{20}	$\nu_{\text{s}}\text{N}_3$	1317 m	1312 [0.3]	1274 (297.7) [0.4]	1288 (482.0) [0.6]
	ν_{21}	$\nu_{\text{s}}\text{N}_3$	1236 m	1227 [0.3]	1218 (334.8) [0.9]	1230 (405.8) [0.7]
	ν_{22}	δN_3			632 (30.5) [5.1]	626 (30.3) [3.7]
	ν_{23}	δN_3			611 (7.5) [2.3]	616 (16.1) [0.5]
	ν_{24}	δN_3			547 (9.0) [0.5]	555 (2.1) [2.5]
	ν_{25}	δN_3			524 (3.8) [0.2]	524 (4.7) [0.5]
	ν_{26}	$\nu_{\text{as}}\text{TeN}_2 \text{ eq}$	[c]	343 [4.6]	381 (67.9) [12.3]	381 (72.7) [13.9]
	ν_{27}	$\nu_{\text{as}}\text{TeN}_2 \text{ ax}$	[c]	307 [2.1]	355 (251.6) [2.6]	358 (228.1) [0.7]
	ν_{28}		[c]	262 [1.2]	242 (7.0) [12.2]	245 (17.4) [4.8]
	ν_{29}		[c]		170 (3.3) [3.0]	216 (18.2) [0.4]
	ν_{30}		[c]		160 (7.3) [2.0]	126 (2.2) [1.5]
	ν_{31}		[c]		91 (1.4) [2.0]	88 (1.5) [1.6]
	ν_{32}		[c]		66 (0.8) [1.7]	82 (2.5) [3.2]
	ν_{33}		[c]		21 (1.2) [7.6]	36 (0.0) [8.7]

[a] Relative IR and Raman intensities are given in parentheses and brackets, respectively. [b] IR intensities in km mol^{-1} and Raman intensities in $\text{\AA}^4 \text{amu}^{-1}$. [c] Not observed, IR spectrum was recorded only between 4000 and 400 cm^{-1} .

Table 2: Comparison of Observed and Unscaled Calculated Vibrational Frequencies (cm^{-1}) and Intensities for $[\text{Te}(\text{N}_3)_6]^{2-}$

mode	approx. mode description		observed ^[a]		calculated ^[b] (in p g S_6)
	in point group C_1		IR	Raman	(IR) [Raman]
a	ν_1	$\nu_{\text{as}}\text{N}_3$	2111 w	2116 [4.2]	2133 a_g (0) [435.5]
	ν_2	$\nu_{\text{as}}\text{N}_3$	2082 m	2085 [1.7]	2101 e_g (0) [938.9]
	ν_3	$\nu_{\text{as}}\text{N}_3$	2063 m	2075 [1.3]	
	ν_4	$\nu_{\text{as}}\text{N}_3$		2065 [0.7]	
	ν_5	$\nu_{\text{as}}\text{N}_3$	2048 s	2057 [0.4]	2094 e_u (7957) [0]
	ν_6	$\nu_{\text{as}}\text{N}_3$	1998 vs		2085 a_u (1205) [0]
	ν_7	$\nu_s\text{N}_3$		1334 [0.6]	1329 e_g (0) [93.9]
	ν_8	$\nu_s\text{N}_3$	1294 mw	1313 [0.6]	
	ν_9	$\nu_s\text{N}_3$		1277 [0.7]	1329 a_g (0) [79.2]
	$\nu_{10,11}$	$\nu_s\text{N}_3$	1251 mw	1260 [0.4]	1324 e_u (652.0) [0]
	ν_{12}	$\nu_s\text{N}_3$	1241 mw		1318 a_u (124.7) [0]
	ν_{13}	δN_3		654 [1.4]	619 e_u (10.3) [0]
	ν_{14}	δN_3		647 [0.9]	
	ν_{15}	δN_3		639 [0.5]	617 a_u (5.2) [0]
	$\nu_{16,17}$	δN_3			616 e_g (0) [23.0]
	ν_{18}	δN_3			613 a_g (0) [5.0]
	$\nu_{19,20}$	δN_3			596 e_u (8.3) [0]
	$\nu_{21,22}$	δN_3			595 e_g (0) [8.5]
	ν_{23}	δN_3			594 a_g (0) [0.5]
	ν_{24}	δN_3			591 a_u (19.7) [0]
	ν_{25}	νTeN_6	[c]	412 [10.0]	310 a_g (0) [174.8]
	ν_{26}	νTeN_6	[c]	385 [1.1]	276 a_u (264.8) [0]
	$\nu_{27,28}$	νTeN_6	[c]		273 e_u (697.3) [0]
	ν_{29}	νTeN_6	[c]	251 [2.9]	259 e_g (0) [146.7]
	ν_{30}	νTeN_6	[c]	229 [2.7]	
	ν_{31}		[c]		155 a_u (17.8) [0]
	$\nu_{32,33}$		[c]		154 e_g (0) [26.0]
	$\nu_{34,35}$		[c]		148 e_u (111.4) [0]
	ν_{36}		[c]		135 a_g (0) [10.9]
	ν_{37}		[c]		115 a_g (0) [15.8]
	$\nu_{38,39}$		[c]		99 e_u (61.2) [0]
	$\nu_{40,41}$		[c]		82 e_g (0) [28.1]
	ν_{42}		[c]		75 a_u (42.4) [0]
	ν_{43}		[c]		41 a_u (8.5) [0]
	$\nu_{44,45}$		[c]		35 e_g (0) [57.4]

ν_{46}	[c]	29 a_g (0) [25.0]
$\nu_{47,48}$	[c]	28 e_u (22.3) [0]
ν_{49}	[c]	23 a_u (2.6) [0]
$\nu_{50,51}$	[c]	18 e_u (4.0) [0]

[a] Relative IR and Raman intensities are given in parentheses and brackets, respectively. [b] IR intensities in km mol^{-1} and Raman intensities in $\text{\AA}^4 \text{amu}^{-1}$. [c] Not observed, IR spectrum was recorded only between 4000 and 400 cm^{-1} .

Figure 1. Raman spectra of solid $\text{Te}(\text{N}_3)_4$.

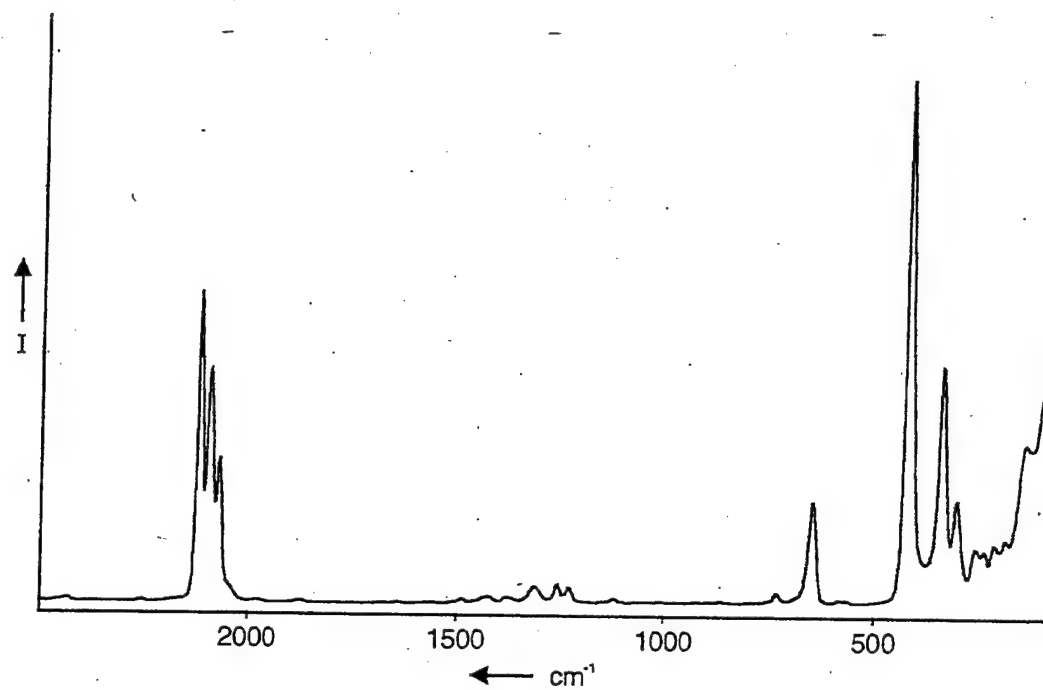
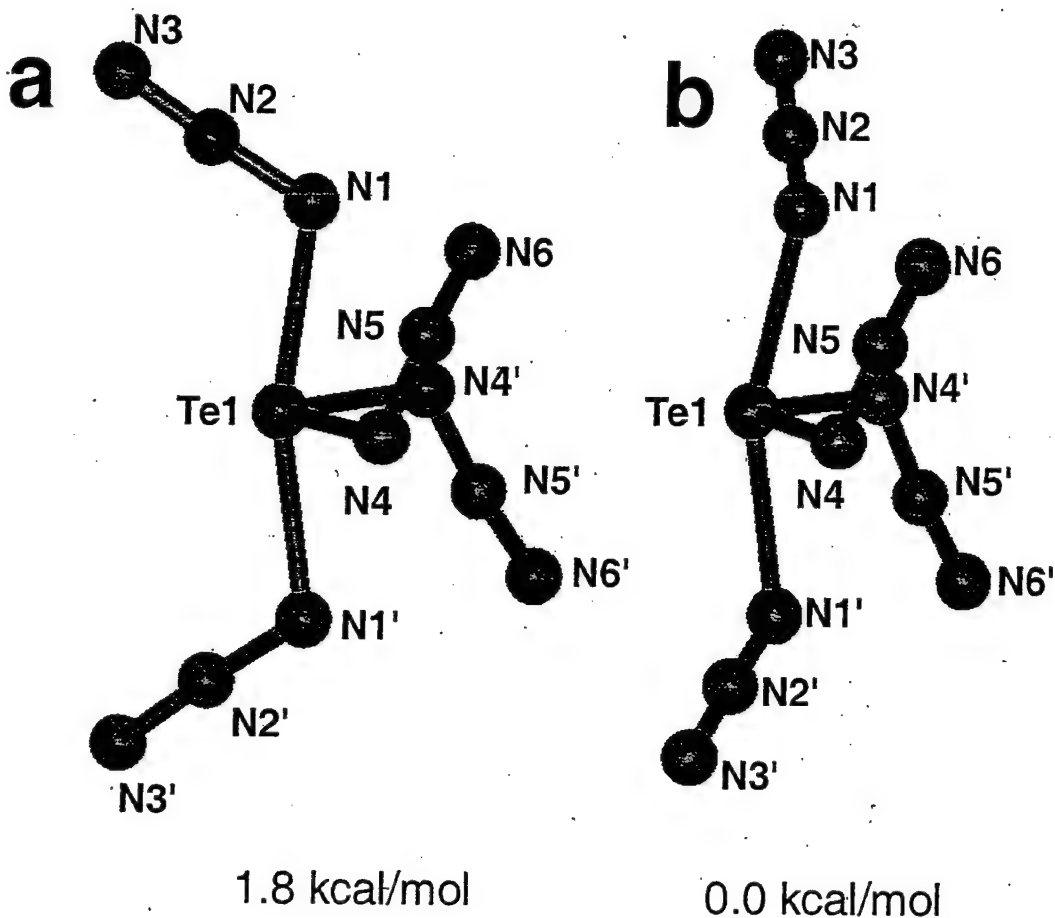


Figure 2. The two minimum energy structures, calculated for $\text{Te}(\text{N}_3)_4$ at the B3LYP/SBKJC+(d) level of theory.



- a) $R(\text{Te1-N1}) = 2.185$, $R(\text{N1-N2}) = 1.251$, $R(\text{N2-N3}) = 1.166$, $R(\text{Te1-N4}) = 2.071$,
 $R(\text{N4-N5}) = 1.267$, $R(\text{N5-N6}) = 1.155$, $\alpha(\text{N1-Te1-N4}) = 89.7$, $\alpha(\text{N4-Te1-N4}') = 100.7$,
 $\alpha(\text{Te1-N1-N2}) = 114.0$, $\alpha(\text{Te1-N4-N5}) = 116.5$, $\alpha(\text{N1-N2-N3}) = 176.2$, $\alpha(\text{N4-N5-N6}) = 172.7$
- b) $R(\text{Te1-N1}) = 2.167$, $R(\text{N1-N2}) = 1.247$, $R(\text{N2-N3}) = 1.164$, $R(\text{Te1-N4}) = 2.080$,
 $R(\text{N4-N5}) = 1.264$, $R(\text{N5-N6}) = 1.155$, $\alpha(\text{N1-Te1-N4}) = 85.0$, $\alpha(\text{N4-Te1-N4}') = 111.7$,
 $\alpha(\text{Te1-N1-N2}) = 117.6$, $\alpha(\text{Te1-N4-N5}) = 119.0$, $\alpha(\text{N1-N2-N3}) = 176.2$, $\alpha(\text{N4-N5-N6}) = 173.0$

Figure 3. ORTEP drawing of the dianionic part of the crystal structure of $[P(C_6H_5)_4]_2[Te(N_3)_6]$. Thermal ellipsoids are shown at the 50 % probability level. Selected bond lengths [\AA] and angles [$^\circ$]: Te-N1 2.132(2), Te-N4 2.241(2), Te-N7 2.093(2), Te-N10 2.419(2), Te-N13 2.199(2), Te-N16 2.530(2), N1-N2 1.229(2), N2-N3 1.117(3), N16-N17 1.197(3), N17-N18 1.152(3), N1-N2-N3 174.4(3), N16-N17-N18 177.6(3), Te-N10-N11 109.18(17), Te-N4-N5 121.20(17), N1-Te-N16 75.07(8), N7-Te-N10 80.64(8), N1-Te-N7 83.47(9), N4-Te-N7 83.72(9), N1-Te-N13 84.18(8), N7-Te-N13 85.23(8), N10-Te-N13 87.91(8), N1-Te-N4 88.92(9), N13-Te-N16 90.37(8), N4-Te-N10 95.88(8), N4-Te-N16 97.84(8), N10-Te-N16 120.36(8).

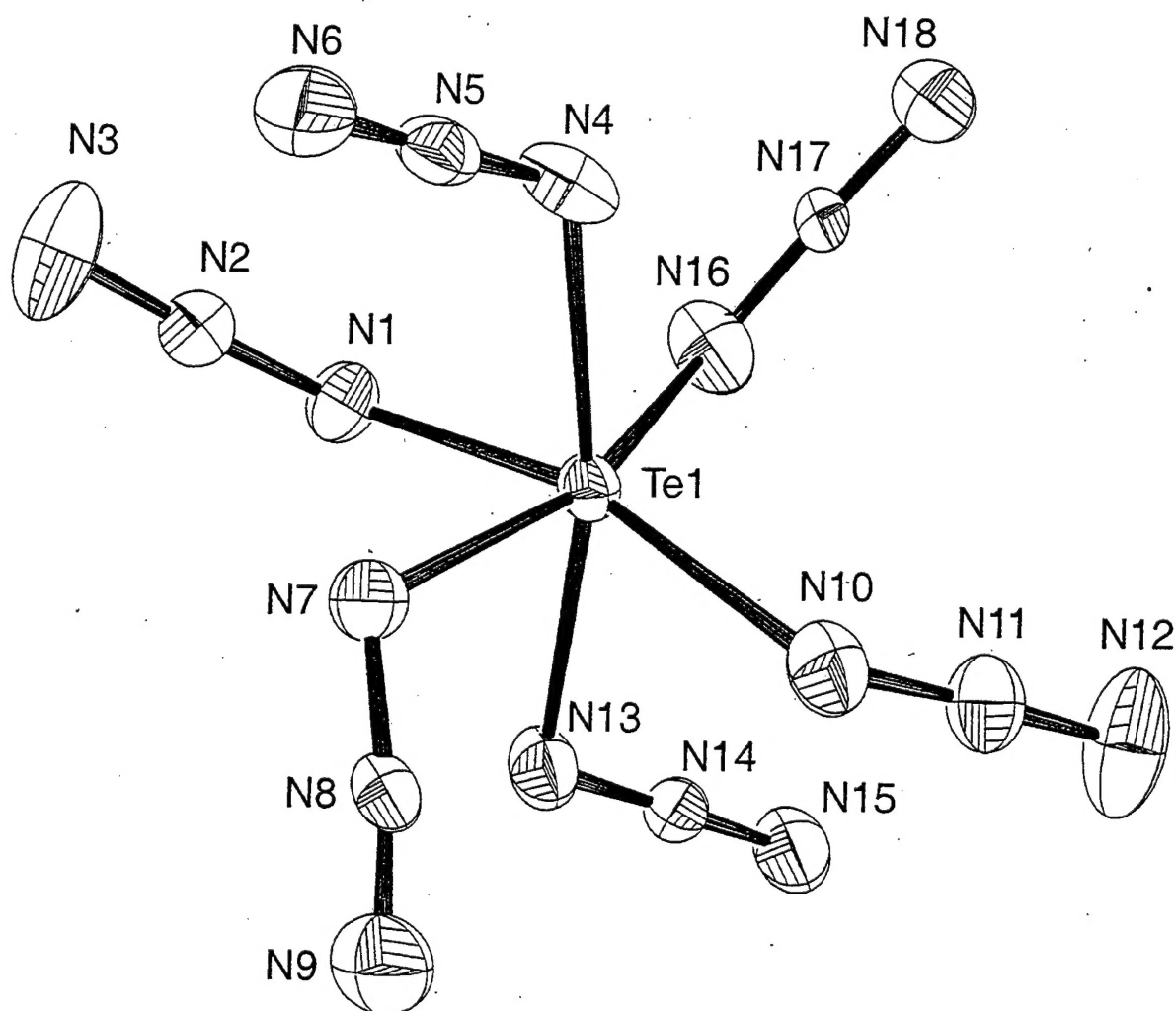
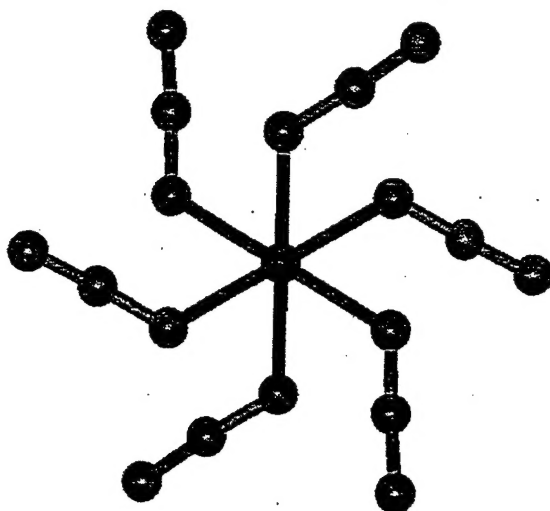
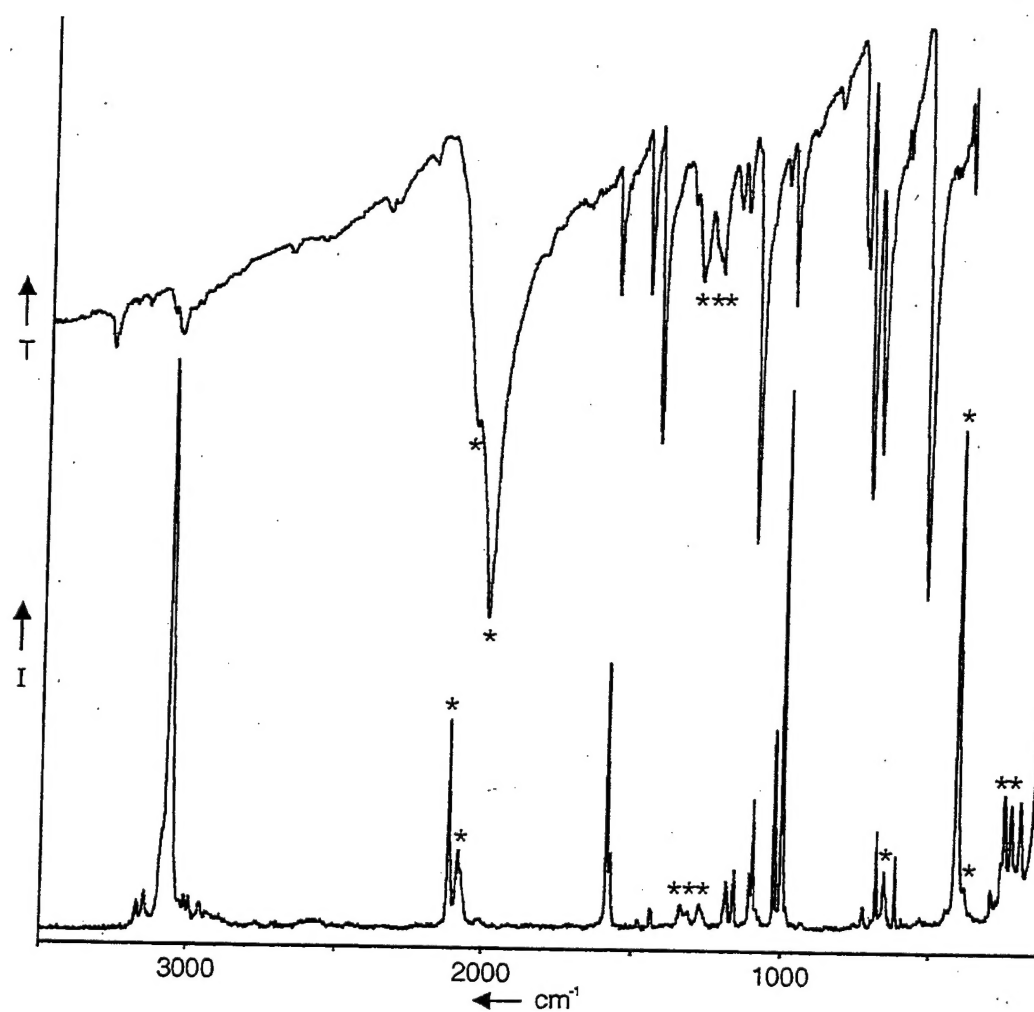


Figure 4. Minimum energy structures of S_6 symmetry predicted at the B3LYP/SBKJC+(d) level of theory for $[\text{Te}(\text{N}_3)_6]^{2-}$ and $\text{Te}(\text{N}_3)_6$ (values in parentheses are for $\text{Te}(\text{N}_3)_6$).



$R(\text{Te}-\text{N}\alpha) = 2.321(2.113)$, $R(\text{N}\alpha-\text{N}\beta) = 1.231(1.258)$, $R(\text{N}\beta-\text{N}\gamma) = 1.179(1.157)$,
 $\alpha(\text{Te}-\text{N}\alpha-\text{N}\beta) = 120.4(115.5)$, $\alpha(\text{N}\alpha-\text{N}\beta-\text{N}\gamma) = 176.2(174.5)$

Figure 5. IR and Raman spectra of $[P(C_6H_5)_4]_2[Te(N_3)_6]$. The bands belonging to the $[Te(N_3)_6]^{2-}$ anion are marked with asterisks.



Synopsis

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Gerken, S. Schneider, T. Schroer,
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Polyazide Chemistry. Preparation
and Characterization of $\text{Te}(\text{N}_3)_4$
and $[\text{P}(\text{C}_6\text{H}_5)_4]_2[\text{Te}(\text{N}_3)_6]$

Highly explosive $\text{Te}(\text{N}_3)_4$ was prepared from the F^- ion catalyzed reaction of TeF_6 with $(\text{CH}_3)_3\text{SiN}_3$ and converted to the more stable $[\text{P}(\text{C}_6\text{H}_5)_4]_2[\text{Te}(\text{N}_3)_6]$ salt by reaction with $[\text{P}(\text{C}_6\text{H}_5)_4][\text{N}_3]$. The sterically active free valence electron pair of Te strongly distorts the structure of the $[\text{Te}(\text{N}_3)_6]^{2-}$ anion from the predicted ideal S_6 symmetry, giving rise to different azide ligands ranging from highly covalent to semi-ionic.

